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Contraction Kinetics of Stretched Polymers via Local Conformational Changes

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ABSTRACT: We use the beginning coefficients in exact time power series to study the kinetics of the stretched conformation-to-random coil contraction of a model polymer system. We treat a two-dimensional (2-d) lattice polymer where each unit can exist in the cis or trans state, the stretched conformation corresponding to the all-trans state. We allow only local conformational changes that do not perturb the chain beyond a small finite range. The mechanism of contraction then becomes the diffusion of cis states into the chain from the ends. Because of the diffusion mechanism we expect power-law behavior of the form $t^{1/2}$ (this form is supported by exactly soluble models). We give exact series for short chains and the asymptotic series for very long chains. We find that the $t^{1/2}$ behavior is truly asymptotic and does not dominate the early behavior as determined by the series.

1. Introduction

We consider the kinetics of the equilibration process whereby a polymer chain, originally in the stretched, extended conformation, contracts to a random chain, as illustrated in Figure 1. We will treat a 2-d lattice polymer with fixed valence angle on the plane-square lattice. For our model the allowed conformations about a bond are the cis and trans conformations shown in Figure 2. Two consecutive cis states are forbidden by excluded volume; longer range exclusion effects could be included, but we will consider only the nearest-neighbor case. For this model the length of the extended structure in Figure 1 is, of course, proportional to L, the number of links in the chain, while the rms end-to-end distance for the random chain varies as $L^{1/2}$.

The effect that we want to incorporate into the kinetics of the process shown in Figure 1 is that cis-to-trans conversions involving motions of large pieces of the chain, such as illustrated in Figure 3, are ruled out (these kinds of moves being improbable because of the extensive perturbation on the solvent structure required). Instead we allow only small local changes that move a local portion of the chain. The moves we will allow are shown in Figure 4. These changes can be described by the following reactions:

From the ends:

$$\mathrm{tt}\ldots \leftrightarrow \mathrm{ct}\ldots$$

$$\mathrm{ttt}\ldots \leftrightarrow \mathrm{tct}\ldots \tag{1.1}$$

Interior moves:

$$\ldots\mathrm{tt(tct)tt}\ldots \leftrightarrow \ldots\mathrm{tc(tct)ct}\ldots$$

$$\ldots\mathrm{tc(tct)tt}\ldots \leftrightarrow \ldots\mathrm{tt(tct)ct}\ldots$$

$$\ldots\mathrm{tc(tct)ct}\ldots \leftrightarrow \ldots\mathrm{tt(tct)tt}\ldots \tag{1.2}$$

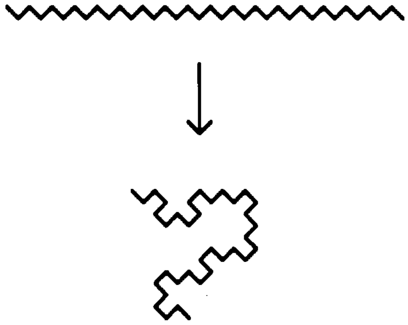

Figure 1. Schematic illustration of the contraction of a fiber from the initial all-trans state to the random coil.

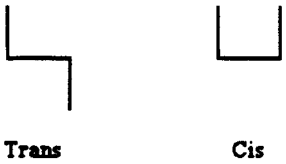

Figure 2. The two conformational states, cis and trans, for each unit of the chain.

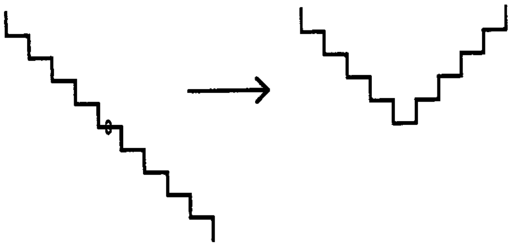

Figure 3. Illustration of a trans → cis isomerization in the interior of a chain that makes a very large change in the total shape of the molecule. Such large changes are forbidden in the present model.

If the above moves are the only conformational changes allowed, then the equilibration process in Figure 1 must proceed by diffusion of cis states into the chain from the ends, as illustrated in Figure 5. Thus the contraction process in this model involves successive randomness evolving at the ends of the chain and diffusing into the chain, as shown in Figure 6. It is the dynamics of this process that we want to investigate.

A large number of different techniques have been used to study the dynamics of polymer chains.[1] Models for polymer motion, such as reptation, allowing only local conformational changes, have been studied using Monte Carlo techniques.[2] We are interested here in the general question of how fast entropy diffuses into an initially ordered system. An example of such a system is the helix–coil transition in poly(amino acids) where one starts with the helical conformation and then perturbs the system so that the final state is the random coil. Helix–coil kinetics

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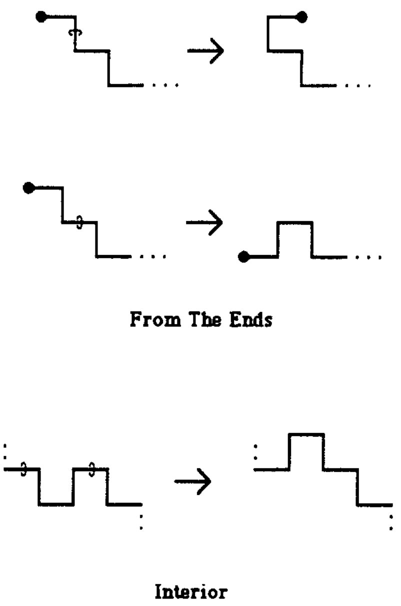

Figure 4. Allowed local conformational changes in the present model.

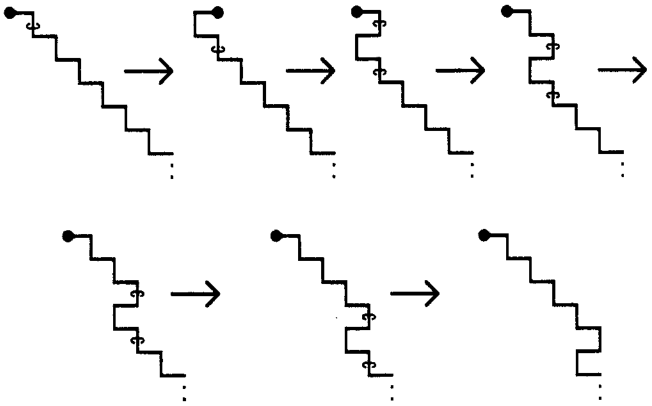

Figure 5. Diffusion of cis states into the interior of a molecule by a succession of local conformational changes.

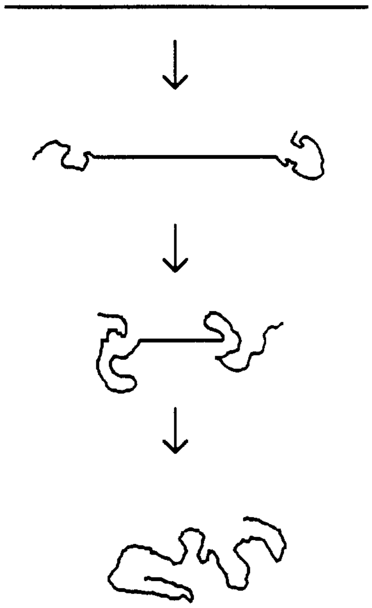

Figure 6. Schematic illustration of the contraction process via the diffusion of randomness into the chain from the ends.

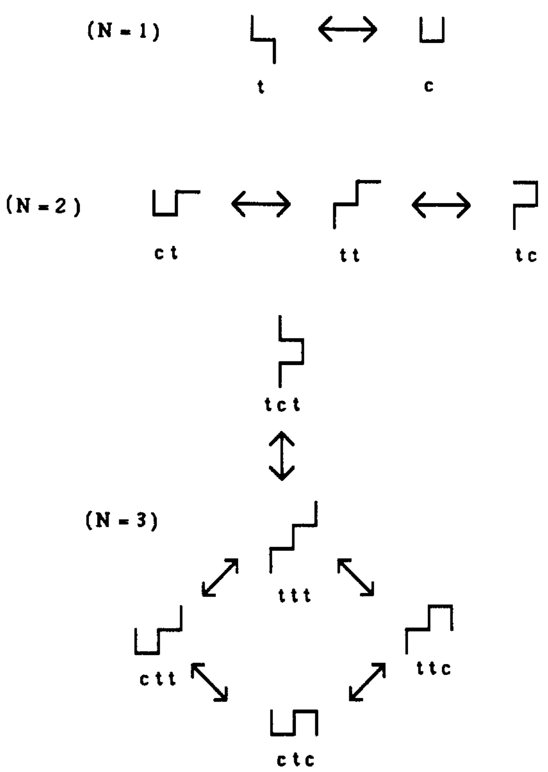

Figure 7. The allowed conformational changes for short chains.

have been treated by Ferretti, Ninham, and Parsegian,[3] by Silverberg and Simha,[4] and by Schwarz and Poland,[5] among others. The general problem of the kinetics of a sequence of first-order reactions has been investigated by Ninham, Nossal, and Zwanzig.[6] In the present work we will use exact time-power series, obtaining a finite number of the coefficients in the appropriate series.[7] In the next section we obtain the exact solution for short chains and then, in the following section, the beginning terms of the exact asymptotic series for long chains. Because our model involves the diffusion of cis states into the chain from the ends, we expect the asymptotic behavior to be a power law of the form $t^{1/2}$. In Appendix A we give some exactly soluble models supporting this functional form. The equilibrium distribution of cis states in the molecule is treated in Appendix B. The series are analyzed in section 4 followed by a brief discussion in section 5.

2. Exact Kinetics for Short Chains

If L is the number of links in our model chain, then $N = L - 2$ is the number of bonds about which one can have cis/trans isomerization. The possible conformational transitions for our model are shown in Figure 7 for N = 1, 2, 3, and 4. The allowed pathways for N = 1–4 are outlined in Figure 8, while the pathways for N = 5 and N = 6 are shown in Figures 9 and 10, respectively.

We define a row vector whose elements are the probabilities of the various species

$$\mathbf{p} = (p_1, p_2, p_3, ..., p_N) \tag{2.1}$$

For given N, the number of distinct species, Ω_N, is given by the recursion relation[8]

$$\Omega_N = \Omega_{N-1} + \Omega_{N-2}$$
$$\Omega_1 = 2, \quad \Omega_2 = 3 \tag{2.2}$$

giving, for N = 1–6, Ω_N = 2, 3, 5, 8, 13, and 21 (the Fibonacci series). As can be seen by examining Figures 8–10, the probabilities of several species will be identical by symmetry if we start out with the all-trans state. From Figures 8–10 one sees that the maximum number of independent probabilities for N = 1–6 are M = 2, 2, 4, 5, 9, and 12.

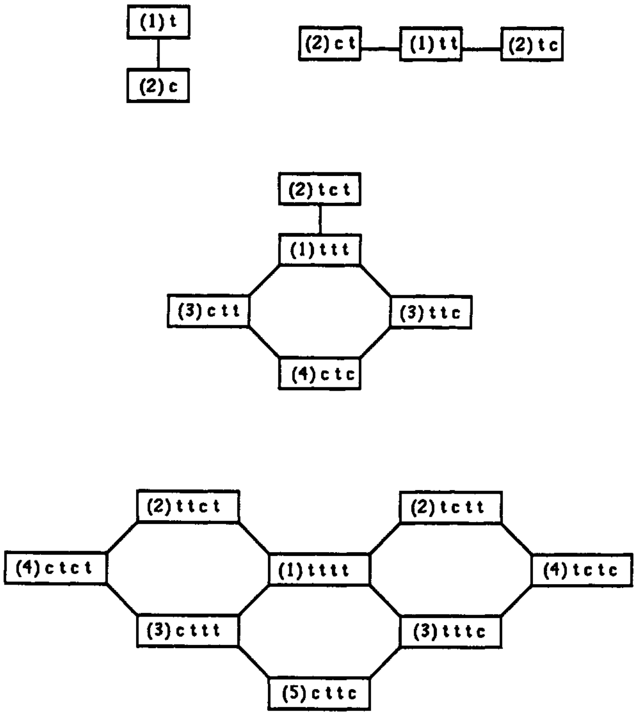

Figure 8. Schematic illustration of the allowed transitions between species for short chains (N = 1, 2, 3, and 4). Each line represents a reversible conformational change. The numbers in parentheses give the species number; a species number is repeated if two species are identical by symmetry (starting from the all-trans state).

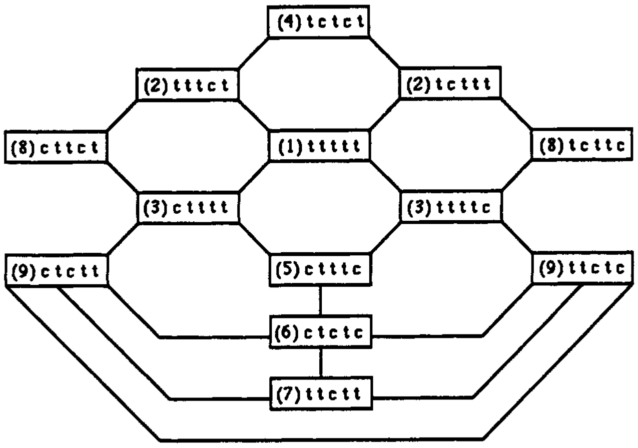

Figure 9. The allowed conformational transitions, as in Figure 8, for N = 5.

The kinetics can be written in the form of a set of coupled first-order reactions linking the various species

$$d\mathbf{p}/dt = -\mathbf{pK} \tag{2.3}$$

where the matrix $\mathbf{K}$ has the structure

$$\mathbf{K} = (k_{ij})$$

$$k_{ij} = -1 \quad \text{if the transition } i \rightarrow j \text{ is allowed}$$

$$k_{ij} = 0 \quad \text{if the transition } i \rightarrow j \text{ is forbidden}$$

$$k_{jj} = -\sum_{i=1(\neq j)}^{M} k_{ij} \tag{2.4}$$

The matrix $\mathbf{K}$ in (2.3) is defined with a minus sign so that the eigenvalues of $\mathbf{K}$ will be positive. Whether or not a particular transition is allowed is determined from the structure of the graphs in Figures 8–10.

The matrices for N = 1–6 are (where the numbers for the row and column indices are the species numbers in Figures 8–10)

$$\mathbf{K}_1 = \begin{array}{c|cc} & 1 & 2 \\ \hline 1 & 1 & -1 \\ 2 & -1 & 1 \end{array} \tag{2.5}$$

$$\mathbf{K}_2 = \begin{array}{c|cc} & 1 & 2 \\ \hline 1 & 2 & -1 \\ 2 & -2 & 1 \end{array} \tag{2.6}$$

$$\mathbf{K}_3 = \begin{array}{c|cccc} & 1 & 2 & 3 & 4 \\ \hline 1 & 3 & -1 & -1 & 0 \\ 2 & -1 & 1 & 0 & 0 \\ 3 & -2 & 0 & 2 & -2 \\ 4 & 0 & 0 & -1 & 2 \end{array} \tag{2.7}$$

$$\mathbf{K}_4 = \begin{array}{c|ccccc} & 1 & 2 & 3 & 4 & 5 \\ \hline 1 & 4 & -1 & -1 & 0 & 0 \\ 2 & -2 & 2 & 0 & -1 & 0 \\ 3 & -2 & 0 & 3 & -1 & -2 \\ 4 & 0 & -1 & -1 & 2 & 0 \\ 5 & 0 & 0 & -1 & 0 & 2 \end{array} \tag{2.8}$$

$$\mathbf{K}_5 = \begin{array}{c|ccccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ \hline 1 & 4 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & -2 & 3 & 0 & -2 & 0 & 0 & 0 & -1 & 0 \\ 3 & -2 & 0 & 4 & 0 & -2 & 0 & 0 & -1 & -1 \\ 4 & 0 & -1 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 5 & 0 & 0 & -1 & 0 & 3 & -1 & 0 & 0 & 0 \\ 6 & 0 & 0 & 0 & 0 & -1 & 4 & -1 & 0 & -1 \\ 7 & 0 & 0 & 0 & 0 & 0 & -1 & 3 & 0 & -1 \\ 8 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 2 & 0 \\ 9 & 0 & 0 & -1 & 0 & 0 & -2 & -2 & 0 & 3 \end{array} \tag{2.9}$$

$$\mathbf{K}_6 = \begin{array}{c|cccccccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\ \hline 1 & 4 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & -2 & 4 & 0 & -2 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 \\ 3 & -2 & 0 & 4 & 0 & -2 & 0 & 0 & -1 & -1 & 0 & 0 & 0 \\ 4 & 0 & -1 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 5 & 0 & 0 & -1 & 0 & 4 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 6 & 0 & 0 & 0 & 0 & -2 & 3 & 0 & 0 & -1 & -1 & 0 & 0 \\ 7 & 0 & -1 & 0 & 0 & 0 & 0 & 4 & 0 & -1 & 0 & -1 & -1 \\ 8 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 3 & 0 & 0 & -1 & 0 \\ 9 & 0 & 0 & -1 & 0 & 0 & -1 & -1 & 0 & 5 & 0 & -1 & -1 \\ 10 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 2 & 0 & -1 \\ 11 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & -1 & 0 & 4 & -1 \\ 12 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & -1 & -1 & -1 & 4 \end{array} \tag{2.10}$$

The secular equations of the above matrices are

$$(N = 1) \qquad \lambda(\lambda - 2) = 0$$

$$(N = 2) \qquad \lambda(\lambda - 3) = 0$$

$$(N = 3) \qquad \lambda(-\lambda^3 + 8\lambda^2 - 18\lambda + 10) = 0$$

$$(N = 4) \qquad \lambda(\lambda^4 - 13\lambda^3 + 58\lambda^2 - 105\lambda + 64) = 0$$

$$(N = 5) \qquad \lambda(\lambda^8 - 28\lambda^7 + 329\lambda^6 - 2108\lambda^5 + 7998\lambda^4 - 18\,208\lambda^3 + 23\,890\lambda^2 - 16\,036\lambda + 3952) = 0$$

$$(N = 6) \qquad \lambda(-\lambda^{11} + 43\lambda^{10} - 819\lambda^9 + 9103\lambda^8 - 65\,459\lambda^7 + 318\,954\lambda^6 - 1\,071\,451\lambda^5 + 2\,473\,147\lambda^4 - 3\,829\,176\lambda^3 + 3\,770\,255\lambda^2 - 2\,112\,840\lambda + 506\,688) = 0 \tag{2.11}$$

The time variation of any average property of the system (for example, the number of cis states or the rms end-to-end distance) can be expressed in the form

$$\Delta = \sum_{m=1}^{M} a_m e^{-\lambda_m t} \tag{2.12}$$

where Δ is scaled so that $\Delta(t=0) = 1$ and $\Delta(t=\infty) = 0$. If

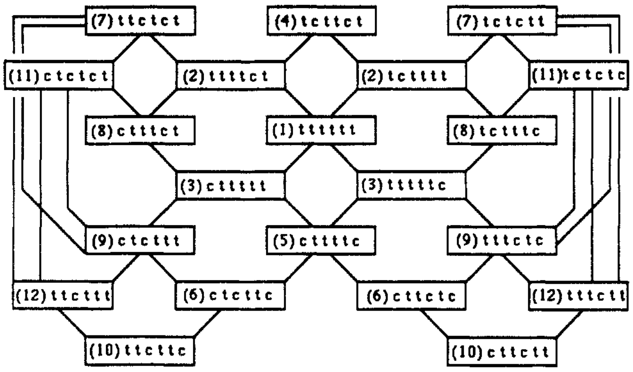

Figure 10. The allowed conformational transitions, as in Figure 8, for $N = 6$.

Table I
Eigenvalues of the Kinetic Matrices for Several Short Chains

$N = 1$	$N = 2$	$N = 3$	$N = 4$	$N = 5$	$N = 6$
2	3	0.830	1.284	0.531	0.866
		2.689	2.517	1.629	1.673
		4.481	3.437	2.361	1.678
			5.763	3.075	2.708
				4.000	3.179
				4.461	3.912
				5.331	4.782
				6.611	5.274
					5.328
					6.390
					7.209

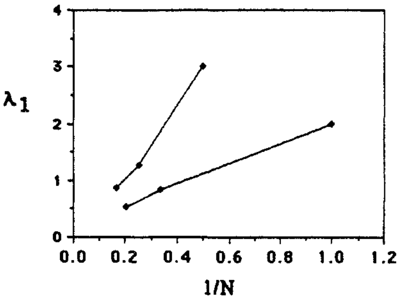

Figure 11. The smallest nonzero eigenvalues of the matrix $\mathbf{K}_N$ for $N = 1$–6 (obtained from eqs 2.11 or Table I) as a function of $1/N$.

λ_1 is the smallest nonzero eigenvalue, then the long-time behavior will be

$$\Delta \sim \exp(-\lambda_1 t) \tag{2.13}$$

Now, since the mechanism of change in our model is diffusion of cis states in from the ends of the chain, as illustrated in Figure 5, we expect relaxation functions in the model to have the form (for large N)

$$\Delta \sim t^{-\gamma} \tag{2.14}$$

where, from analogy with diffusion and random walk models, we expect $\gamma = {}^1/_2$ (or some simple variant thereon). To obtain the form of (2.14) for large N, $\lambda_1(N)$ must approach zero. The roots of the secular equations given in (2.11) are shown in Table I. The quantity $\lambda_1(N)$ is plotted for $N = 1$–6 as a function of $1/N$ in Figure 11. One sees that there are two curves, one for odd values of N and the other for even values. The curves clearly are consistent with $\lambda_1 \to 0$ as $N \to \infty$.

Throughout this work we will take the following initial conditions (taking species number one as the all-trans state)

$$p_1(0) = 1 \quad \text{(all-trans state)}$$

$$p_m(0) = 0 \quad (m \geq 2) \tag{2.15}$$

With the initial conditions of (2.15), the species probabilities for $N = 1$ and $N = 2$ are (using the species labeling of Figure 8)

$N = 1$:

$$p_1 = \frac{1}{2} + \frac{1}{2}e^{-2t}$$

$$p_2 = \frac{1}{2} - \frac{1}{2}e^{-2t}$$

$N = 2$:

$$p_1 = \frac{1}{3} + \frac{2}{3}e^{-3t}$$

$$p_2 = \frac{1}{3} - \frac{1}{3}e^{-3t} \tag{2.16}$$

To construct an average quantity we put the values of the desired quantity for each species in a vector $\mathbf{q}$. Then

$$\langle q \rangle = \mathbf{p} \cdot \mathbf{q} \tag{2.17}$$

(In our scheme where two species may be equal in probability by symmetry, one must then multiply the corresponding element in $\mathbf{q}$ by a factor of 2 so as to count the total weight of the species properly.)

For example, for the rms end-to-end distance one requires the quantity $R_m^2 = x_0^2 + y_0^2$ (where x_0 and y_0 are the x and y distances between the two ends of a particular conformation). Table II shows the values of R_m^2 for the various species for $N = 1$–6. Using these numbers, one can then construct $\langle R^2 \rangle$, obtaining, for example, for $N = 1$ and $N = 2$

$$(N = 1) \qquad \langle R^2 \rangle = R_1^2 p_1 + R_2^2 p_2$$

$$= 3 + 2e^{-2t} \tag{2.18}$$

$$(N = 2) \qquad \langle R^2 \rangle = R_1^2 p_1 + 2R_2^2 p_2$$

$$= (16/3) + (8/3)e^{-3t} \tag{2.19}$$

It is more convenient to introduce a function that is unity at $t = 0$ and zero at $t = \infty$. For $\langle R^2 \rangle$ on has

$$\Delta_R = \frac{\langle R^2 \rangle - \langle R^2 \rangle_e}{R_0^2 - \langle R^2 \rangle_e} \tag{2.20}$$

where R_0^2 is the length of the all-trans conformation and $\langle R^2 \rangle_e$ is the equilibrium rms end-to-end distance. For $N = 1$–6 one has $\langle R^2 \rangle_e = 3$, (16/3), (37/5), 10, (165/13), and (328/21) = 3, 5.33, 7.4, 10, 12.69, and 15.62, respectively. Using the above numbers, one obtains

$$(N = 1) \qquad \Delta_R = e^{-2t}$$

$$(N = 2) \qquad \Delta_R = e^{-3t}$$

$$(N = 3) \qquad \Delta_R = 0.107e^{-0.830t} + 0.288e^{-2.689t} + 0.605e^{-4.481t}$$

$$(N = 4) \qquad \Delta_R = 0.076e^{-1.284t} + 0.091e^{-2.517t} + 0.484e^{-3.437t} + 0.349e^{-5.763t} \tag{2.21}$$

Table II
Square of the End-to-End Distance for the Different Short-Chain Conformations

species	$N = 1$	$N = 2$	$N = 3$	$N = 4$	$N = 5$	$N = 6$
1	5	8	13	18	25	32
2	1	4	9	10	17	20
3			5	10	13	20
4			5	10	17	8
5				2	9	8
6					9	8
7					9	20
8					5	16
9					13	20
10						4
11						16
12						16

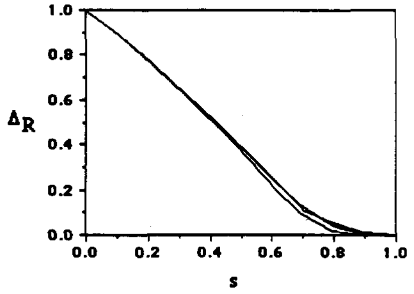

Figure 12. The function Δ_R, defined in (2.20) and given in (2.21) for $N = 1, 2, 3$, and 4. The scaled time, discussed following (2.21), is used; the independent variable is $s = t/(1 + t)$, which maps the whole time axis onto the unit line. The curves for $N = 1$ and $N = 2$ are identical and represent simple exponential decay.

To compare these functions, it is useful to scale the time so that $(d\Delta/dt)_{t=0} = -1$ for all of them. This involves introducing a new time variable $t' = \alpha t$; for $N = 1$–4 one has $\alpha = 2$, 3, 3.57, and 4. The relaxation functions in (2.21), so scaled, are shown in Figure 12. Since Δ_R for $N = 1$ and $N = 2$ are simple exponentials in t', i.e., $\Delta_R = \exp(-t')$, one can see that the relaxation functions for $N = 3$ and $N = 4$, by comparison, are not very different from simple exponential decay.

Having described the exact relaxation functions for short chains, we now turn to the opposite extreme, the relaxation when the chain is so long that one can consider the two ends independent (at least for the initial stages of the contraction process).

3. Series Expansions for Long Chains

In the previous section we treated exactly, for short chains, the equilibration process from the all-trans state to the equilibrium population of conformations when the allowed paths were determined by local conformational changes such as those illustrated in Figures 7–10. In this section we turn our attention to very long chains where we can consider the two ends to be independent for the initial phase of the equilibration process.

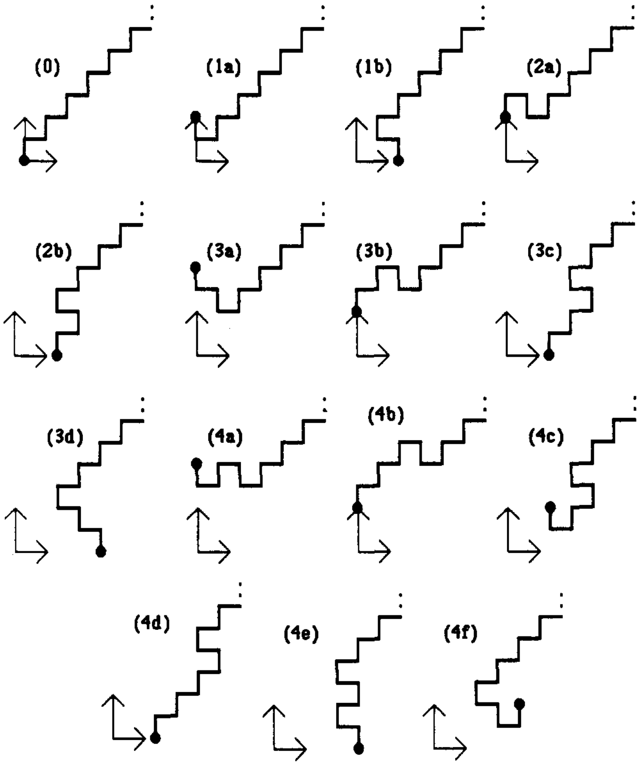

Figure 13. Successive stages of contraction of the left end of a long chain originally in the all-trans state (species (0)). The labels, 1_i, 2_j, etc., refer to all possible distinct conformations evolved via 1, 2, etc., steps, respectively, from the all-trans state. The solid dot represents the free end of the chain. The coordinate arrows represent the original position of the end.

Figure 13 shows the conformation of the left end of a chain (the solid dot indicates the free end of the chain while the dashes indicate the continuation of the chain) that results from a maximum of four allowed steps in the contraction process. The arrows indicate the origin of the chain at time equal zero for each conformation. The kinetics again can be represented by eq 2.3, except that now the matrix increases without bound for an infinite chain. Figure 14 shows the branching tree of connections between the species given in Figure 13; each line represents a reversible transition between the appropriate species. The matrix that incorporates the transitions shown in Figure 14 is given below (with the labeling introduced in Figure 13); the determination of the diagonal elements for species 4a–4f requires the construction of the next level of the branching hierarchy. The row and column indices are the species number, following the order given in Figure 13.

$$\mathbf{K} = \begin{pmatrix} 2 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 2 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 2 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 3 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 3 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 2 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 3 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 4 & 0 & 0 & 0 & -1 & -1 & -1 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 0 & -1 & -1 \\ 0 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 & 4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \tag{3.1}$$

Using (2.3), one can calculate the derivatives of $\mathbf{p}$ evaluated at $t = 0$

$$(d^n\mathbf{p}/dt^n)_{t=0} = \mathbf{p}_0(-\mathbf{K})^n \tag{3.2}$$

A given matrix **K** that includes all conformations generated through n moves will give the exact first n derivatives for a chain long enough that after n moves at each end, the two ends remain independent. By examining Figure 13, one finds that at most $2n$ links have been moved for n steps in the contraction process. Thus one can use **K** to calculate the first n derivatives for unwinding from both ends if the total number of links is greater than $2n$ (this takes into account unwinding from both ends: n moves will at most involve $2n$ links independent of how the moves are divided up between the two ends; the maximum at any one end is $2n$).

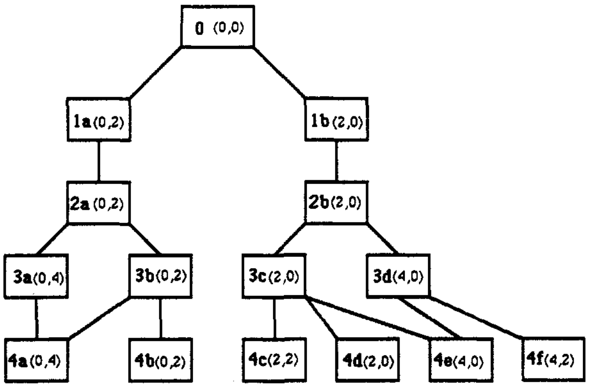

Figure 14. The allowed transitions between the species given in Figure 13. Each line represents a reversible conformational transition. The numbers in parentheses give the (x,y) coordinates of the end of the chain, (0,0) being the coordinates for the original all-trans state. Species 4f represents a cul de sac, the only transition available being the reverse reaction. Note that the species divide into two distinct branches, a divergence that persists at least through $n = 6$.

If $\langle q \rangle$ is any ensemble average for the system, then the power series in time for $\langle q \rangle$ is given by

$$\langle q \rangle = \sum_{n=0}^{\infty} q_n t^n / n! \tag{3.3}$$

or

$$q_n = \mathbf{p}_n \cdot \mathbf{q} \tag{3.4}$$

where $\mathbf{q}$ is the vector of q values for the various species and $\mathbf{p}_n$ is the vector of nth derivatives for the various species.

The numbers in parentheses in Figure 14 are the (x,y) coordinates of the new position of the left end of the chain (taking the origin as the original end of the all-trans state). Using these numbers, one can calculate $\langle x \rangle$, $\langle y \rangle$, $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle R^2 \rangle$, the latter quantity being the rms distance of the end from the original position of the left end. We have obtained the series through $n = 6$. We find

$$\langle x \rangle = 2t - 6t^2/2! + 22t^3/3! - 84t^4/4! + 328t^5/5! - 1306t^6/6! + \ldots \tag{3.5}$$

$$\langle y \rangle = 2t - 6t^2/2! + 22t^3/3! - 80t^4/4! + 282t^5/5! - 950t^6/6! + \ldots \tag{3.6}$$

$$\langle x^2 \rangle = 4t - 12t^2/2! + 52t^3/3! - 224t^4/4! + 944t^5/5! - 3900t^6/6! + \ldots \tag{3.7}$$

$$\langle y^2 \rangle = 4t - 12t^2/2! + 52t^3/3! - 216t^4/4! + 852t^5/5! - 3196t^6/6! + \ldots \tag{3.8}$$

$$\langle R^2 \rangle = 8t - 24t^2/2! + 104t^3/3! - 440t^4/4! + 1796t^5/5! - 7096t^6/6! + \ldots \tag{3.9}$$

One sees that the series for $\langle x \rangle$ and $\langle y \rangle$ and the series for $\langle x^2 \rangle$ and $\langle y^2 \rangle$ are the same through $n = 3$; one can see that this should be so from the symmetry of the branching pattern shown in Figure 14: through $n = 3$, x and y moves are symmetric, but for $n > 3$ this symmetry ceases to hold. Although the series for the moments of x and y are not exactly the same to all orders, one expects the two sets of moments to behave in essentially the same fashion.

Using the above series, one can calculate the dimensions of a chain of L links with independent conformational diffusion from both ends. By using simple geometry, one has (see Figure 15—the x and y moves are calculated relative to the (x,y) coordinates shown)

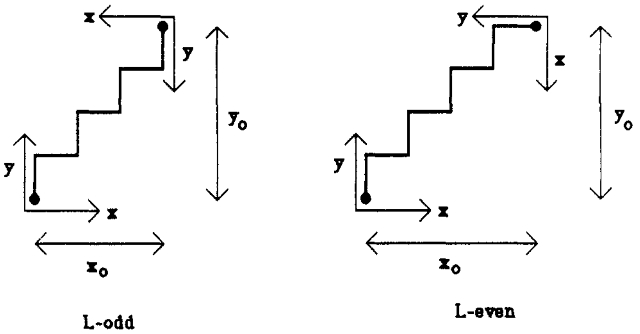

Figure 15. The coordinate system used to calculate $\langle R^2 \rangle$ for odd and even number of links in the chain.

L odd:

$$\langle X \rangle = x_0 - 2\langle x \rangle$$

$$\langle Y \rangle = y_0 - 2\langle y \rangle \tag{3.10}$$

L even:

$$\langle X \rangle = x_0 - \langle x \rangle - \langle y \rangle$$

$$\langle Y \rangle = y_0 - \langle y \rangle - \langle x \rangle \tag{3.11}$$

where x_0 and y_0 are the original x and y distances between the two ends:

$$x_0 = |L/2|$$

$$y_0 = |(L + 1)/2| \tag{3.12}$$

where the vertical bars indicate that one is to take the integral part of the enclosed quantity.

The rms end-to-end distance for the chain is constructed as follows. We treat the case for L odd. For the case where the chain is in conformational state i on the left end and in conformational state j on the right end, one has

$$R_{ij}^2 = X_{ij}^2 + Y_{ij}^2 \tag{3.13}$$

where

$$X_{ij} = x_0 - x_i - x_j \tag{3.14}$$

$$Y_{ij} = y_0 - y_i - y_j \tag{3.15}$$

where

$$\sum_i p_i = 1, \qquad \sum_i \sum_j p_i p_j = 1 \tag{3.16}$$

Using the above relations, one obtains (following a similar procedure for L even)

L odd:

$$\langle R^2 \rangle = R_0^2 - 4x_0\langle x \rangle - 4y_0\langle y \rangle + 2\langle x^2 \rangle + 2\langle x \rangle^2 + 2\langle y^2 \rangle + 2\langle y \rangle^2 \tag{3.17}$$

L even:

$$\langle R^2 \rangle = R_0^2 - 2x_0\langle x \rangle - 2x_0\langle y \rangle + 2\langle x^2 \rangle + 4\langle x \rangle\langle y \rangle - 2y_0\langle x \rangle - 2y_0\langle y \rangle + 2\langle y^2 \rangle \tag{3.18}$$

For the first six terms given in (3.5)–(3.9), these relations give the exact $\langle R^2 \rangle$ for chains longer than $2n = 12$. In general, this procedure gives the exact n terms for $\langle R^2 \rangle$

if

$$L > 2n \tag{3.19}$$

We can use the matrices of section 2 to calculate the exact expansions for $\langle R^2 \rangle$ for short chains and compare those results with the results obtained by using (3.17) or (3.18). One has

$N = 1$:

exact: $\langle R^2 \rangle = 5 - 4t + 8t^2/2! - 16t^3/3! + ...$

series: $\langle R^2 \rangle = 5 - 8t + 56t^2/2! - 344t^3/3! + ...$

$N = 2$:

exact: $\langle R^2 \rangle = 8 - 8t + 24t^2/2! - 72t^3/3! + ...$

series: $\langle R^2 \rangle = 8 - 16t + 80t^2/2! - 432t^3/3! + ...$

$N = 3$:

exact: $\langle R^2 \rangle = 13 - 20t + 80t^2/2! - 336t^3/3! + ...$

series: $\langle R^2 \rangle = 13 - 24t + 104t^2/2! - 520t^3/3! + ...$

$N = 4$:

exact: $\langle R^2 \rangle = 18 - 32t + 144t^2/2! - 704t^3/3! + ...$

series: $\langle R^2 \rangle = 18 - 32t + 128t^2/2! - 608t^3/3! + ...$

$N = 5$:

exact: $\langle R^2 \rangle = 25 - 40t + 152t^2/2! - 664t^3/3! + ...$

series: $\langle R^2 \rangle = 25 - 40t + 152t^2/2! - 696t^3/3! + ...$

$N = 6$:

exact: $\langle R^2 \rangle = 32 - 48t + 176t^2/2! - 760t^3/3! + ...$

series: $\langle R^2 \rangle = 32 - 48t + 176t^2/2! - 784t^3/3! + ...$

(3.20)

In addition to the distance statistics, one can also calculate the average number of cis states that diffuse into the molecule, both the net number and the probability that a given unit is cis. For the net number of cis states entering the chain from one end one finds (here the signs do not necessarily regularly alternate)

$$\langle n_{\text{cis}} \rangle = 2t - 4t^2/2! + 8t^3/3! - 2t^4/4! - 125t^5/5! + 1157t^6/6! + ... \tag{3.21}$$

The probability that the first and second units, respectively, are in the cis state is given by

$$p_{1\text{-cis}} = t - 3t^2/2! + 8t^3/3! - 15t^4/4! - 12t^5/5! + 363t^6/6! + ... \tag{3.22}$$

$$p_{2\text{-cis}} = t - 3t^2/2! + 8t^3/3! - 17t^4/4! + 7t^5/5! + 247t^6/6! + ... \tag{3.23}$$

4. Analysis of Series

We begin with the series of (3.9) for $\langle R^2 \rangle$, which we repeat here for convenience

$$\langle R^2 \rangle = 8t - 24t^2/2! + 104t^3/3! - 440t^4/4! + 1796t^5/5! - 7096t^6/6! + ... \tag{3.9}$$

Scaling the time so that $t' = 8t$, one obtains (where we drop the prime on the time for simplicity)

$$\langle R^2 \rangle = t - 0.1875t^2 + 0.03385t^3 - 4.476 \times 10^{-3}t^4 + 4.567 \times 10^{-4}t^5 - 3.760 \times 10^{-5}t^6 + ... \tag{4.1}$$

In general, given a function of x expressed in a time series

$$f(x) = \sum_{n=1}^{\infty} c_n x^n \tag{4.2}$$

we define the ratios of successive coefficients as follows:

$$r_n = c_n/c_{n-1} \tag{4.3}$$

If $f(x)$ has a singularity of the form

$$f(x) \sim \left(\frac{1}{1 - x/x_\sigma}\right)^\gamma \tag{4.4}$$

then if the singularity at $x = x_\sigma$ is the closest singularity to the origin, and hence determines the radius of convergence of the series in (4.2), the ratios will have the asymptotic form[9]

$$r_n \sim \frac{1}{x_\sigma}\left[1 + \frac{1}{n}(\gamma - 1)\right] \tag{4.5}$$

Forming the ratios of the successive coefficients in (4.1), one obtains the series of numbers (for r_2 to r_6) −0.1875, −0.1806, −0.1322, −0.1020, and −0.0823. When plotted as a function of $(1/n)$, these extrapolate smoothly to $t_\sigma^{-1} = 0$, indicating that the radius of convergence of the time series is infinite (as is the case, for example, for the function $\exp(-t)$).

We will use two procedures in this section to put the series in a more useful form. First, given a general function expressed as a time power series

$$r = \sum_{n=1}^{\infty} a_n t^n \tag{4.6}$$

this can be inverted to give t as a function of r

$$t = \sum_{n=1}^{\infty} b_n r^n \tag{4.7}$$

If $t \rightarrow \infty$ as $r \rightarrow \infty$, then it is convenient to introduce the Euler transform

$$w = \frac{r}{1 + r}, \qquad r = \frac{w}{1 - w} \tag{4.8}$$

which moves the singularity down to $w_\sigma = 1$. We will use the r/w notation throughout this section.

For the function $\langle R^2 \rangle = r$ one has

$$t = r + 0.1875r^2 + 0.0364r^3 + 5.697 \times 10^{-3}r^4 + 3.265 \times 10^{-4}r^5 - 2.118 \times 10^{-4}r^6 + ... \tag{4.9}$$

We will see that this type of inverted series is usually very well-behaved; the example in (4.9) is an exception, with a switch of sign at the last term given in the series. Moving on to the w series, we do obtain a very uniform expansion

$$t = w + 1.1875w^2 + 1.4115w^3 + 1.678w^4 + 1.992w^5 + 2.360w^6 + \dots \tag{4.10}$$

The ratios of successive coefficients in this series (giving r_2 to r_6) are 1.1875, 1.1886, 1.1885, 1.1873, and 1.1851. These numbers are about as uniform as one could expect to find in this type of numerical analysis. The only problem is that they extrapolate smoothly to a value of approximately $w_\sigma^{-1} = 1.17$, or $w_\sigma = 0.855$. Since we expect $\langle R^2 \rangle \sim t$ from the random walk analogy, we anticipate that

$$t \sim 1/(1 - w) \tag{4.11}$$

that is, $w_\sigma = 1$ and the ratios should be independent of n and extrapolate to w_σ^{-1} with zero slope. The ratios are quite constant in value and they do extrapolate to a value very close to one, but the discrepancy is real and interesting. We will try to understand why this happens using our random walker model as a guide. But first we examine the other series that we have obtained.

The series for $\langle x \rangle$ is given in (3.5)

$$\langle x \rangle = 2t - 6t^2/2! + 22t^3/3! - 84t^4/4! + 328t^5/5! - 13066t^6/6! + \dots \tag{3.5}$$

Scaling time by setting $t' = 2t$ (and again dropping the prime), we have

$$\langle x \rangle = t - 0.75t^2 + 0.4583t^3 - 0.2188t^4 + 0.0854t^5 - 0.02834t^6 + \dots \tag{4.12}$$

The ratios are −0.75, −0.6111, −0.4773, −0.3905, and −0.3318, which, as with the ratios for (4.1), extrapolate to $t_\sigma^{-1} = 0$, indicating again an infinite radius of convergence for the time series. We expect, again from the random walk analogy, that $\langle x \rangle \sim t^{1/2}$. From the above results we see that $\langle x \rangle$ does not have the asymptotic form (expecting $\gamma = {}^1/_2$)

$$\langle x \rangle \sim (a + t)^\gamma \tag{4.13}$$

since in that case we would find a finite radius of convergence, i.e., $t_\sigma = -a$.

Taking $r = \langle x \rangle$, the inverted series becomes

$$t = r + 0.75r^2 + 0.6667r^3 + 0.6094r^4 + 0.5448r^5 + 0.4595r^6 + \dots \tag{4.14}$$

while the w series is

$$t = w + 1.75w^2 + 3.1667w^3 + 5.859w^4 + 10.9823w^5 + 20.6938w^6 + \dots \tag{4.15}$$

The ratios of the latter series are 1.75, 1.810, 1.850, 1.874, and 1.884. Again the ratios are very uniform but extrapolate to the wrong value (approximately $w_\sigma^{-1} = 1.95$). From the square root asymptotic form just discussed, we expect

$$t \sim \left(\frac{1}{1 - w}\right)^2 \tag{4.16}$$

that is, the ratios should extrapolate to $w_\sigma^{-1} = 1$ with a slope of one. So again we have a result that needs clarification by the random walk model.

We next turn to the kinetics of diffusion of cis states into the interior of the chain via the ends. The probability that the first unit in the chain is in the cis state is given by (3.22)

$$p_{1\text{-cis}} = t - 1.5t^2 + 1.333t^3 - 0.625t^4 - 0.1t^5 + 0.5042t^6 + \dots \tag{4.17}$$

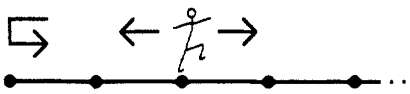

Figure 16. Model of a random walker on a 1-d lattice. The chain extends to plus infinity on the right, but the walker must turn around at the left end (reflection).

Taking $r = p_{1\text{-cis}}$, the inverted series is

$$t = r + 1.5r^2 + 3.1667r^3 + 7.5r^4 + 18.933r^5 + 49.692r^6 + \dots \tag{4.18}$$

The ratios for this series are 1.5, 2.111, 2.368, 2.524, and 2.625. In (B.17) we gave the probability as 0.382 that the first unit in a long chain is cis. Thus we expect $r_\sigma^{-1} = 1/0.382 = 2.62$ and we see that the ratios quoted above are moving in that direction (although, in the range for which we have data, they appear to be headed in the direction of overshooting the mark).

The time power series for the total average number of cis states in the molecule is given by (3.21)

$$\langle n_{\text{cis}} \rangle = t - (1/2)t^2 + (1/6)t^3 - 0.005208t^4 - 0.03255t^5 + 0.02511t^6 + \dots \tag{4.19}$$

Taking $r = \langle n_{\text{cis}} \rangle$, the inverted series is

$$t = r + (1/2)r^2 + (1/3)r^3 + 0.2135r^4 + 0.1315r^5 + 0.07059r^6 + \dots \tag{4.20}$$

while the w series is

$$t = w + 1.5w^2 + 2.333w^3 + 3.7135w^4 + 5.9857w^5 + 9.6969w^6 + \dots \tag{4.21}$$

The ratios for the w series are 1.5, 1.556, 1.592, 1.612, and 1.620. The numbers extrapolate to about $w_\sigma^{-1} = 1.68$. But again, from the asymptotic form of (4.16), we expect that $\langle n_{\text{cis}} \rangle \sim t^{1/2}$ and that the ratios should extrapolate to $w_\sigma^{-1} = 1$ with a slope of one.

For comparison we turn now to the exactly soluble models discussed in Appendix A. First we examine the details of the random walker model illustrated in Figure 16. The average distance attained by the walker is given by (A.6). The series expansion of that result is

$$\begin{aligned}\langle n \rangle &= t - t^2/2! + 2t^3/3! - 5t^4/4! + 14t^5/5! - 42t^6/6! + 132t^7/7! - 429t^8/8! + 1430t^9/9! - 4862t^{10}/10! + \dots \\ &= t - (1/2)t^2 + (1/3)t^3 - 0.20833t^4 + 0.11567t^5 - 0.05833t^6 + 0.02619t^7 - 0.01064t^8 + 0.003941t^9 - 0.001340t^{10} + \dots\end{aligned} \tag{4.22}$$

Taking $r = \langle n \rangle$, the inverted series is (there is no r^4 term)

$$t = r + (1/2)r^2 + (1/6)r^3 - 0.0333r^5 - 0.00972r^6 + 0.00992r^7 + 0.00858r^8 - 0.00109r^9 - 0.00506r^{10} + \dots \tag{4.23}$$

One sees that there is uniformity of sign in the above series. The pattern of a band of positive signs followed by a band of negative signs, and so on, usually is indicative of a singularity in the complex r plane. One obtains a very well-behaved series if one introduces an Euler transform into the t series of (4.22)

$$s = \frac{t}{1 + t}, \qquad t = \frac{s}{1 - s} \tag{4.24}$$

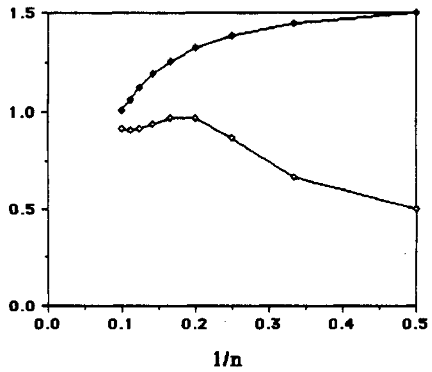

Figure 17. Ratios of successive coefficients of series for the random walker model of Figure 16. The open symbols (bottom curve) refer to the ratios for (4.25) while the solid symbols (top curve) refer to the ratios for (4.26).

Using the above change of variable, (4.22) becomes

$$\langle n\rangle = s + (1/2)s^2 + (1/3)s^3 + 0.29167s^4 + 0.28333s^5 + 0.27500s^6 + 0.25952s^7 + 0.23936s^8 + 0.21879s^9 + 0.20090s^{10} + \dots \quad (4.25)$$

One also obtains a uniform series by converting (4.23) to the w series

$$t = w + 1.5w^2 + 2.1667w^3 + 3w^4 + 3.9667w^5 + 4.9903w^6 + 5.951w^7 + 6.7072w^8 + 7.1342w^9 + 7.2023w^{10} + \dots \quad (4.26)$$

Since we know that $\langle n\rangle \sim t^{1/2}$, we know that the above series have the following asymptotic forms:

$$\text{(4.25):}\quad \langle n\rangle \sim \left(\frac{1}{1-s}\right)^{1/2}$$

$$\text{(4.26):}\quad t \sim \left(\frac{1}{1-w}\right)^{2} \quad (4.27)$$

Thus we expect that the ratios of the successive coefficients in both (4.25) and (4.26) will extrapolate to unity, the ratios approaching one with a slope of minus one-half (4.25) and one (4.26). The ratios for the two series are shown in Figure 17, plotted as a function of $(1/n)$. Both sets of data do clearly seem to be extrapolating to one, but one is unable to extract from these data a precise value of the characteristic exponent associated with the random walk, namely $^1/_2$. Since it is very difficult to obtain exact series expansions for models such as our cis/trans polymer model (which, unlike the present simple random walk model, has no known exact solution) much beyond the tenth term or so, it is unlikely that analysis of series will suffice to accurately determine asymptotic behavior.

Finally we turn to the model of 1's diffusing into the end of a half-infinite 1-d lattice. The probability that the initial lattice site (labeled site zero) is in state one is given by (A.20). The explicit series expansion is

$$p_0 = t - 3t^2/2! + 10t^3/3! - 35t^4/4! + 126t^5/5! - 462t^6/6! + 1716t^7/7! - 6435t^8/8! + 24310t^9/9! - 92378t^{10}/10! + \dots \quad (4.28)$$

Taking $r = p_0$, the inverted series is

$$t = r + 1.5r^2 + 2.833r^3 + 5.833r^4 + 12.533r^5 + 27.582r^6 + 61.573r^7 + 138.65r^8 + 313.84r^9 + 712.32r^{10} + \dots \quad (4.29)$$

Since we know that $p_0 \rightarrow {}^1/_2$ as $t \rightarrow \infty$, we have the asymptotic form

$$(1/2 - p_0) \sim t^{-1/2} \quad (4.30)$$

or

$$t \sim \left(\frac{1}{1-2p_0}\right)^2$$

Thus we expect the radius of convergence of the r series in (4.29) to be $r_\sigma = {}^1/_2$ and hence the ratios for the series should extrapolate to $r_\sigma^{-1} = 2$. The appropriate ratios are 1.5, 1.889, 2.059, 2.149, 2.201, 2.232, 2.252, 2.263, 2.270. Clearly, the ratios are close to the required value of 2, but at this stage (through $n = 10$) they are not yet moving directly to the precise value of 2. Thus the rate of convergence of diffusion series to the known asymptotic behavior is very slow indeed. Presumably this is why we earlier found that while the inverted series often were very well-behaved, they did not give precisely the expected asymptotic behavior.

The exact formula for the total number of 1's that have diffused onto the lattice is given by (A.22). The first ten terms of the series are

$$\langle n_1\rangle = t - 2t^2/2! + 6t^3/3! - 20t^4/4! + 70t^5/5! - 252t^6/6! + 924t^7/7! - 3432t^8/8! + 12870t^9/9! - 48620t^{10}/10! + \dots \quad (4.31)$$

Letting $r = \langle n_1\rangle$, the inverted and w series are

$$t = r + r^2 + r^3 + 0.8333r^4 + 0.41667r^5 - 0.2333r^6 - 0.9389r^7 - 1.3399r^8 - 0.9829r^9 + 0.4294r^{10} + \dots \quad (4.32)$$

$$t = w + 2w^2 + 4w^3 + 7.8333w^4 + 14.8333w^5 + 26.2733w^6 + 46.8305w^7 + 93.5004w^8 + 212.124w^9 + 503.98w^{10} + \dots \quad (4.33)$$

Since we know that $\langle n_1\rangle \sim t^{1/2}$, we know that (4.33) must have the asymptotic form of (4.16); in particular, the radius of convergence of the series is one. The ratios for (4.33) are 2, 2, 1.958, 1.894, 1.771, 1.782, 1.997, 2.269, and 2.376. Once again, the ratios are well-behaved but are not yet moving toward the known value of one. So again we see that series for diffusion problems are very slow to converge to their asymptotic limits.

5. Discussion

In this paper we have treated the kinetics of contraction of a polymer chain initially in the all-trans state (stretched conformation). By restricting the allowed conformational changes to local moves that alter only a small portion of the molecule, the mechanism of contraction is essentially a diffusion of cis states into the end of the chain followed by a reversible random walk down the molecule. For a limited range of exclusion (only nearest-neighbor cis states are forbidden) one expects typical random walk results ($\langle R^2\rangle \sim t$, $\langle n_{\text{cis}}\rangle \sim t^{1/2}$). We have seen that when the time power series are inverted to give the series

$$t = \sum a_n r^n$$

$$t = \sum b_n w^n$$

$$w = r/(1 + r) \quad (5.1)$$

(where r is the average quantity of interest), these series are very well-behaved, giving smoothly varying ratios. However, the ratios do not allow one to determine the characteristic exponents for the asymptotic behavior. By computing the ratios for similar but exactly soluble random walk models, we found that the ratios for those systems also did not permit the known asymptotic behavior to be determined from 10 or so terms in a power series. Thus

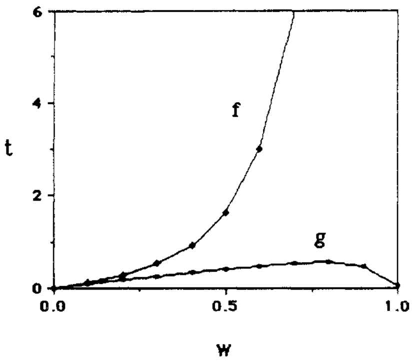

Figure 18. The functions $f(w)$ and $g(w)$ for the random walker model. The functions are defined in eq (5.2).

it seems that this kind of series analysis does not permit an independent determination of the asymptotic form.

However, if we assume that the asymptotic form is known, finite series can be used to construct practical relaxation functions. As an example let us take the case of the random walker of Figure 16. The average distance, $\langle n \rangle$, that the walker has gone from the origin (the analog of the x component of the end of our stretched macromolecule) is given exactly by (A.6). The series expansion for the same quantity is given in (4.22), while the inverted series, giving t as a function of w is given in (4.26) (where $r = \langle n \rangle/(1 + \langle n \rangle)$ and $w = r/(1 + r)$). From (A.8) we know that $\langle n \rangle \sim t^{1/2}$ and hence $t \sim (1/(1 - w))^2$, as indicated in (4.27). Thus we write

$$t = f(w) = g(w)\left(\frac{1}{1-w}\right)^2 \tag{5.2}$$

If one knows the series for $f(w)$, then one can construct the series for $g(w)$:

$$g(w) = w - (1/2)w^2 + (1/6)w^3 + (1/6)w^4 + (2/15)w^5 + 0.05694w^6 - 0.06230w^7 - 0.2057w^8 - 0.3286w^9 - 0.3588w^{10} + \ldots \tag{5.3}$$

The function $f(w)$, as given in (5.2), and $g(w)$ are plotted in Figure 18. For the range shown, $f(w)$ from (5.2) and the exact result of (4.6) are superimposable. One sees that $g(w)$ is a slowly varying background function that gives a mild perturbation on the main function, $(1/(1 - w))^2$. The presence of $g(w)$ guarantees that the first ten derivatives are exact; the $(1/(1 - w))^2$ term gives the correct asymptotic functional form. Thus from this example one sees that a finite time power series can be converted into a useful function that describes the relaxation behavior over a wide range of values of the appropriate variable. Of course, to use this procedure one must know the asymptotic form. In constructing Figure 18, we simply used the truncated series for $g(w)$ of (5.3); one could get a better estimate of the series as $w \to 1$ by using a Padé approximant.

For our polymer model we discussed time power series for $\langle R^2 \rangle$ and $\langle n_{\text{cis}} \rangle$. For $\langle R^2 \rangle$, (4.10) gives the appropriate w series; from (4.11) we expect $t \sim (1/(1 - w))$. Hence we assume the form

$$t = f(w) = g(w)\left(\frac{1}{1-w}\right) \tag{5.4}$$

Using the series of (4.11), we find

$$g(w) = w + 0.1875w^2 + 0.2240w^3 + 0.2665w^4 + 0.314w^5 + 0.368w^6 + \ldots \tag{5.5}$$

For $\langle n_{\text{cis}} \rangle$, (4.20) gives the w series; from (4.16) we expect $t \sim (1/(1 - w))^2$. Thus we use the form of (5.2) and obtain

$$g(w) = w - (1/2)w^2 + (1/3)w^3 + 0.5468w^4 + 0.8920w^5 + 1.439w^6 + \ldots \tag{5.6}$$

The $g(w)$ functions of (5.5) and (5.6) both represent small perturbations on the behavior of the appropriate function $f(w)$ that is dominated by the singularities given in (5.4) and (5.2), respectively.

Appendix A. Some Exactly Soluble Random Walk Models for Comparison

For comparison with the series expansions obtained in the previous section it is useful to have some exactly soluble random walk models for similar systems. First we consider the contraction kinetics. The rate of change of the x or y components of the end of the chain, starting from the all-trans state, as illustrated in Figure 1, should be similar to the random walk on the half-infinite 1-d lattice of sites with reflection at the origin. This random walk model is illustrated in Figure 16, where the walker represents the end of the chain. The condition of reflection at the origin indicates that the chain has a maximum length (all-trans state) beyond which it cannot go. The probabilities that the walker is at various lattice sites are governed by the set of differential difference equations

$$\begin{aligned} \mathrm{d}p_0/\mathrm{d}t &= -p_0 + p_1 \\ \mathrm{d}p_1/\mathrm{d}t &= p_0 - 2p_1 + p_2 \\ \mathrm{d}p_2/\mathrm{d}t &= p_1 - 2p_2 + p_3 \end{aligned} \tag{A.1}$$

This set of equations, with the reflecting boundary condition at the zero site, is readily solved using the method of images.[10] The solution is

$$p_n(t) = e^{-2t}[I_n(2t) + I_{n+1}(2t)] \tag{A.2}$$

where I_n is the imaginary Bessel function

$$I_n(2t) = t^n \sum_{m=0}^{\infty} \frac{t^{2m}}{m!(m+n)!} \tag{A.3}$$

The average distance the walker goes from the origin (the analog of the x component by which the end of the macromolecule has contracted) is given by

$$\langle n \rangle = \sum_{n=0}^{\infty} n p_n \tag{A.4}$$

Using the following relations for the imaginary Bessel functions[11]

$$\begin{aligned} nI_n &= t(I_{n-1} - I_{n+1}) \\ I_0 + 2\sum_{n=1}^{\infty} I_n &= e^{2t} \end{aligned} \tag{A.5}$$

one obtains the explicit equation for $\langle n \rangle$

$$\langle n \rangle = e^{-2t}[I_1 + 2t(I_1 + I_2) - (e^{2t} - I_0 - 2I_1)/2] \tag{A.6}$$

The I_n functions have the well-known asymptotic behavior[11]

$$e^{-2t} I_n \sim 1/(4\pi t)^{1/2} \tag{A.7}$$

Combined with the explicit t factor appearing in (A.6), one has the asymptotic form

$$\langle n \rangle \sim t^{1/2} \tag{A.8}$$

a standard random walk result.

The second model system we treat is for the number of cis states diffusing into the molecule. Rather than cis and trans states, we will consider two states, 0 and 1, and consider the diffusion of 1's into the system (as if they were particles undergoing a random walk on the chain). The only rule about the interaction of the particles is that no two 1's can occupy the same site at the same time. For the random walk part of the model, (A.1) describes the probability of having a 1 at site n. (Since (A.1) is strictly applicable to independent walkers only, it is by no means obvious that one can use (A.1) to treat the case where there are lots of 1's on the chain bumping into one another. It can be shown, however, that if the range of exclusion is only a single site, then (A.1) exactly treats the random walks for an arbitrary density right up to close packing. We will offer an alternate derivation of the series as a check on this procedure.) The additional feature that we must treat, since we are interested in the number of 1 states, is that 1's can enter the system (reversibly) only at site zero (this is the analog of the diffusion of cis states into the molecule from the end of the chain as illustrated in Figure 5). This process by itself can be described by the reaction (for site zero only)

$$0 \leftrightarrow 1 \tag{A.9}$$

with the differential equation (p_0 is the probability that site zero is occupied while $(1 - p_0)$ is the probability that the same site is empty)

$$\begin{aligned} \mathrm{d}p_0/\mathrm{d}t &= -p_0 + (1 - p_0) \\ &= 1 - 2p_0 \end{aligned} \tag{A.10}$$

Combining the source rate equation of (A.10) and the random walk equations of (A.1), one has

$$\begin{aligned} \mathrm{d}p_0/\mathrm{d}t &= 1 - 3p_0 + p_1 \\ \mathrm{d}p_1/\mathrm{d}t &= p_0 - 2p_1 + p_2 \\ \mathrm{d}p_2/\mathrm{d}t &= p_1 - 2p_2 + p_3 \end{aligned} \tag{A.11}$$

The boundary condition at the origin (for the p_0 term) is

$$p_{-1} + p_0 = 1 \tag{A.12}$$

If (A.12) always holds, then $\mathrm{d}p_0/\mathrm{d}t = p_{-1} - 2p_0 + p_1$ and one has a simple solution. The only way to make (A.12) hold at all times is to have the condition

$$p_{-n} = 1 - p_{n-1} \quad (\text{all } n \geq 1) \tag{A.13}$$

Since (A.13) must hold at all times, one must have the initial condition

$$p_{-n}(0) = 1, \quad p_{n-1}(0) = 0 \quad (\text{all } n \geq 1) \tag{A.14}$$

The condition of (A.14) represents the infinite 1-d lattice with the following initial condition (full of particles to the left of site zero, empty from zero to plus infinity)

$$\begin{array}{cccccccccc} \ldots & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & \ldots \\ & (-4) & (-3) & (-2) & (-1) & (0) & (1) & (2) & (3) & \end{array} \tag{A.15}$$

where the numbers in parentheses give the lattice site number.

The diffusion of 1's from the left side of the lattice into the right side of the lattice is then exactly the same process as the diffusion of 1's into site zero from a reservoir of constant activity. Thus our problem is simply a random walk problem with the initial condition of (A.15). The conditional probability that a random walker is at site n, having started at site m, $P(m|n)$, is given by

$$P(m|n) = e^{-2t} I_{n-m}(2t) \tag{A.16}$$

Summing over the initial conditions gives

$$p_n(t) = \sum_m p_m(0) P(m|n) \tag{A.17}$$

With the initial conditions of (A.14), one obtains ($I_m = I_{-m}$)

$$p_n(t) = e^{-2t} \sum_{m=-1}^{-\infty} I_{n-m} = e^{-2t} \sum_{k=n+1}^{\infty} I_k \tag{A.18}$$

Using the latter of eqs A.5, one finally obtains

$$p_n = \frac{1}{2} - \frac{1}{2} e^{-2t} I_0 - e^{-2t} \sum_{m=0}^{n} I_m \quad (n \geq 0) \tag{A.19}$$

The first two probabilities are specifically

$$\begin{aligned} p_0 &= \frac{1}{2} - \frac{1}{2} e^{-2t} I_0 \\ p_1 &= \frac{1}{2} - \frac{1}{2} e^{-2t} I_0 - \frac{1}{2} e^{-2t} I_1 \end{aligned} \tag{A.20}$$

The average number of 1 states in the whole molecule as a function of time is

$$\langle n_1 \rangle = \sum_{n=0}^{\infty} p_n \tag{A.21}$$

Using (A.18) and (A.5), we find

$$\langle n_1 \rangle = e^{-2t}[I_1 + t(I_1 + I_2)] \tag{A.22}$$

From (A.7), we again obtain the asymptotic form

$$\langle n_1 \rangle \sim t^{1/2} \tag{A.23}$$

A useful check on the above manipulation of differential difference equations and Bessel functions is obtained by writing down the explicit differential equations linking the various allowed states of the chain. The species, representing the entrance of 1's into the left end of the 1-d lattice and the subsequent diffusion down the molecule, for the first six steps of the process are shown in Figure 19. The differential equations linking these species are (we use the symbol S_m to represent a species and its probability):

$$\begin{gathered} \mathrm{d}S_0/\mathrm{d}t = -S_0 + S_1, \quad \mathrm{d}S_1/\mathrm{d}t = S_0 - 2S_1 + S_2, \\ \mathrm{d}S_2/\mathrm{d}t = S_1 - 3S_2 + S_3 + S_4, \quad \mathrm{d}S_3/\mathrm{d}t = S_2 - 2S_3 + S_5, \\ \mathrm{d}S_4/\mathrm{d}t = S_2 - 3S_4 + S_5 + S_6, \quad \mathrm{d}S_5/\mathrm{d}t = S_3 + S_4 - 4S_5 + \\ S_7 + S_8, \quad \mathrm{d}S_6/\mathrm{d}t = S_4 - 3S_6 + S_8 + S_9, \quad \mathrm{d}S_7/\mathrm{d}t = S_5 - \\ 3S_7 + S_{10} + S_{11}, \quad \mathrm{d}S_8/\mathrm{d}t = S_5 + S_6 - 4S_8 + S_{11} + S_{12}, \\ \mathrm{d}S_9/\mathrm{d}t = S_6 - 3S_9 + S_{12} + S_{13}, \quad \mathrm{d}S_{10}/\mathrm{d}t = S_7 + \ldots, \\ \mathrm{d}S_{11}/\mathrm{d}t = S_7 + S_8 + \ldots, \quad \mathrm{d}S_{12}/\mathrm{d}t = S_8 + S_9 + \ldots, \\ \mathrm{d}S_{13}/\mathrm{d}t = S_9 + \ldots \end{gathered} \tag{A.24}$$

Writing the probability of each species as a power series in time

$$S_m = \sum_{k=0}^{\infty} \alpha_{km} t^k / k! \tag{A.25}$$

the equations in (A.24) represent a set of recursion relations for the α_{km}; the equations in (A.24), part of an infinite hierarchy of such equations, are sufficient to give all average quantities through the sixth term (power of t).

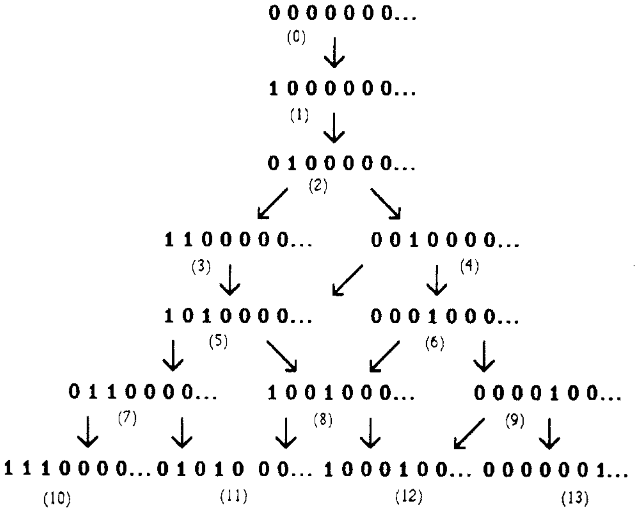

Figure 19. Species and transitions for the model whereby 1's diffusion into the left end of a 1-d lattice and take random walks down the lattice.

Power series for average quantities are obtained by collecting the appropriate S_m terms. Specifically

$$\langle n_1\rangle = S_1 + S_2 + 2S_3 + S_4 + 2S_5 + S_6 + 2S_7 + 2S_8 + S_9 + 3S_{10} + 2S_{11} + 2S_{12} + S_{13} + \ldots \quad \text{(A.26)}$$

$$p_0 = S_1 + S_3 + S_5 + S_8 + S_{10} + S_{12} + \ldots \quad \text{(A.27)}$$

$$p_1 = S_2 + S_3 + S_7 + S_{10} + S_{11} + \ldots \quad \text{(A.28)}$$

Equations A.26, A.27, and A.28 give identically the same results as (A.22) and (A.20), respectively.

Appendix B. Equilibrium Probability Profile for Cis States

In section 3 we gave series for the diffusion of cis states into the end of an all-trans chain. For comparison, it is useful to know what the equilibrium distribution of cis states is as a function of position in the molecule. We use a method originally due to Lacombe and Simha[12] and described in detail by Poland.[13]

We consider a chain having N bonds about which one can have cis/trans isomerization ($N = L - 2$, where L is the number of links). We label the bonds from 1 (left end) to N (right end):

$$(1)(2)(3)....(N-1)(N) \quad \text{(B.1)}$$

In our model a cis state cannot follow a cis state. This means that the conditional probabilities for cis states are (giving the conditional probability that given c, then c or t, respectively, follow)

$$P(\mathrm{c}|\mathrm{c}) = 0$$

$$P(\mathrm{c}|\mathrm{t}) = 1 \quad \text{(B.2)}$$

The above relations hold independent of the location in the chain. For trans states one has the conditional probabilities (which do depend on the location in the chain)

$$P(\mathrm{t}_m|\mathrm{t}_{m+1}) = \alpha_m$$

$$P(\mathrm{t}_m|\mathrm{c}_{m+1}) = 1 - \alpha_m \quad \text{(B.3)}$$

We define the following sequence-dependent a priori probabilities

$$p(\mathrm{c}_m) = \beta_m$$

$$p(\mathrm{t}_m) = 1 - \beta_m \quad \text{(B.4)}$$

Now consider the following two conformational states of the molecule (the dots indicate that the sequence continues in a uniform fashion, here all-trans, to the other end of the molecule):

$$\begin{array}{ll} & \qquad\quad N \\ \text{(I)} & \ldots\mathrm{t}\ \mathrm{t}\ \mathrm{c} \\ \text{(II)} & \ldots\mathrm{t}\ \mathrm{t}\ \mathrm{t} \end{array} \quad \text{(B.5)}$$

The above two sequences can be used to construct the following conditional probabilities

$$P(\mathrm{t}_{N-1}|\mathrm{c}_N) = \frac{q_{\mathrm{I}}}{q_{\mathrm{I}} + q_{\mathrm{II}}} = \frac{1}{2}$$

$$P(\mathrm{t}_{N-1}|\mathrm{t}_N) = \frac{q_{\mathrm{II}}}{q_{\mathrm{I}} + q_{\mathrm{II}}} = \frac{1}{2} \quad \text{(B.6)}$$

where the q's are the appropriate partition functions for the given sequence. Since we take the statistical weights of cis and trans as the same (unity for simplicity—the only cooperative effect we include is that consecutive cis states are forbidden), all of the q's are unity. The result of (B.6) is

$$\alpha_{N-1} = 1/2 \quad \text{(B.7)}$$

Now consider another set of conformations

$$\begin{array}{ll} & \quad m \qquad\qquad N \\ \text{(I)} & \ldots\mathrm{t}\ \mathrm{c}\ \mathrm{t}\ \mathrm{t}\ \mathrm{t}\ \mathrm{t}\ \mathrm{t} \\ \text{(II)} & \ldots\mathrm{t}\ \mathrm{t}\ \mathrm{t}\ \mathrm{t}\ \mathrm{t}\ \mathrm{t}\ \mathrm{t} \end{array} \quad \text{(B.8)}$$

The ratio of the a priori probabilities for these two sequences is

$$\frac{p_{\mathrm{I}}}{p_{\mathrm{II}}} = 1 = \frac{P(\mathrm{t}_m|\mathrm{c}_{m+1})P(\mathrm{c}_{m+1}|\mathrm{t}_{m+2})}{P(\mathrm{t}_m|\mathrm{t}_{m+1})P(\mathrm{t}_{m+1}|\mathrm{t}_{m+2})} = \left(\frac{1-\alpha_m}{\alpha_m}\right)\left(\frac{1}{\alpha_{m+1}}\right) \quad \text{(B.9)}$$

(The sequences are defined so that almost all of the conditional probabilities cancel except the two around site m.) Equation B.9 can be rearranged to give the recursion relation

$$\alpha_m = \left(\frac{1}{\alpha_{m+1} + 1}\right) \quad \text{(B.10)}$$

which starts with (B.7), i.e., $\alpha_{N-1} = {}^1/_2$, and works down to α_1.

For long chains α_m will become independent of m as one moves away from the right end of the molecule. In that limit, setting $\alpha_m = \alpha_{m+1} = \alpha$ in (B.10), one obtains

$$\alpha^2 + \alpha - 1 = 0 \quad \text{(B.11)}$$

or

$$\alpha = (-1 + \sqrt{5})/2 = 0.618034 \quad \text{(B.12)}$$

From (B.10) and (B.7) we know all of the conditional probabilities, the α_m, for a finite chain with arbitrary N.

To calculate the a priori probability of finding a cis state at any site in the molecule we first construct the following two sequences:

$$\begin{array}{ll} & 1 \\ \text{(I)} & \mathrm{c}\ \mathrm{t}\ \mathrm{t}\ldots \\ \text{(II)} & \mathrm{t}\ \mathrm{t}\ \mathrm{t}\ldots \end{array} \quad \text{(B.13)}$$

Table III
Cis Probability Profiles for Various Chain Lengths[a]

m	$N = 2$	$N = 4$	$N = 6$	$N = 10$	$N = 20$
1	0.333	0.375	0.381	0.382	0.382
2	0.333	0.25	0.238	0.236	0.236
3		0.25	0.286	0.292	0.292
4		0.375	0.286	0.271	0.271
5			0.238	0.278	0.279
6			0.381	0.278	0.276
7				0.271	0.277
8				0.292	0.276
9				0.236	0.276
10				0.382	0.276
11					0.276
12					0.276
13					0.276
14					0.277
15					0.276
16					0.279
17					0.271
18					0.292
19					0.236
20					0.382

[a] The numbers give the probability that a unit in the chain is in the cis state; the index m is the position in the chain, while N is the chain length.

for which

$$\frac{p_{\mathrm{I}}}{p_{\mathrm{II}}} = 1 = \frac{p(\mathrm{c}_1)P(\mathrm{c}_1|\mathrm{t}_2)}{p(\mathrm{t}_1)P(\mathrm{t}_1|\mathrm{t}_2)} \tag{B.14}$$

or

$$\left(\frac{\beta_1}{1-\beta_1}\right)\frac{1}{\alpha_1} = 1 \tag{B.15}$$

which can be solved for β_1

$$\beta_1 = \frac{\alpha_1}{1+\alpha_1} \tag{B.16}$$

For long chains $\alpha_1 = \alpha$ (the limiting value given in (B.12)) and β_1 (the probability that the first unit in the chain is cis) has the value

$$\beta_1 = 0.38197 \quad \text{(long-chain limit)} \tag{B.17}$$

Using a basic identity for the probabilities, we have

$$p(\mathrm{c}_{m+1}) = p(\mathrm{c}_m)P(\mathrm{c}_m|\mathrm{c}_{m+1}) + p(\mathrm{t}_m)P(\mathrm{t}_m|\mathrm{c}_{m+1}) \tag{B.18}$$

or

$$\beta_{m+1} = (1-\beta_m)(1-\alpha_m) \tag{B.19}$$

which is a recursion relation for β_{m+1}, which starts with β_1 of (B.16) (which requires that one first calculates the α_m). In the interior of long chains a limiting value of β will be attained. Setting $\beta_{m+1} = \beta_m = \beta$ and taking $\alpha_m = \alpha$ (i.e., using the long-chain limit) gives

$$\beta = \frac{1-\alpha}{2-\alpha} = 0.2764 \quad \text{(interior of long chains)} \tag{B.20}$$

Thus in long chains the probability of a cis state is 0.382 at the end, decreasing to 0.276 in the interior.

Table III gives the exact cis probability profiles for several finite chains.

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